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DIFFERENTIATION OF METEORIC MATTER IN THE EARTH'S ATMOSPHERE

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DIFFERENTIATION OF METEORIC MATTER IN THE EARTH'S ATMOSPHERE

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ABSTRACT. Heating, fusion, and atomization of meteoric bodies in the atmosphere are examined. It is shown that these processes can lead to an appreciable redistribution of elements which in turn leads to substantial changes in the mineralogical and chemical composition of the resulting spherules. The distribution of Ni and Co in the black magnetic spherules originating from the Tunguska fall shows that the coefficient of separation of elements can be very large. Fusion of microscopic particles of ferrous silicates is accompanied by incongruent decomposition into magnetic and silicate phase with subsequent separation of the phases. The content of elements in spherules cannot be used as a cosmogony criterion, owing to the substantial differentiation of matter in the formation of cosmic spherules.

Until recently meteorites were the only representatives of extra- /104**
terrestrial matter that were subjected to a thorough laboratory investigation. At the same time, many researchers pointed out many times that meteorites represent a very small fraction of the total amount of matter falling on the Earth from outer space [1, 2, 3]. Practically more than 99.99% of solid cosmic matter falls on the earth in a finely divided state.

The usual meteorites are observed only when the heaviest bodies, having a small relative velocity with respect to the Earth, fall through the atmosphere. These represent a small fraction of cosmic matter. There are some doubts as to

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**Numbers in the margin indicate the pagination in the original foreign text.

what fraction this represents of the entire extraterrestrial matter.

The basic difficulty involved in the study of incident fine matter is caused by the absence of strict criteria for cosmogenicity. Usually when collecting samples on the surface of the Earth and in the adjoining atmospheric layer, the round smooth shape of particles (cosmic spherules) is used as the criterion of cosmic origin.

It must be kept in mind that the smooth shape cannot serve as a valid criterion of cosmic origin, since this shape may also be assumed by technogenic and volcanogenic spherules. In the present paper we shall discuss the processes that take place during the formation of spherules of extraterrestrial origin.

Two basic mechanisms for the formation of cosmic spherules are possible: a) a melting of a body (or its parts) and solidification of the melted droplets; b) partial or complete vaporization of a body followed by a condensation of the matter contained in the supersaturated vapor. Both of these mechanisms may take place in a number of processes occurring both when meteorites and micrometeors fly through the Earth's atmosphere, and when gigantic meteorites hit the surface of the Earth at great speeds.

It is only the finest particles of extraterrestrial origin that can pass through the atmosphere without melting, and can reach the surface of the Earth, preserving their original shape.

When "fast" micrometeorites pass through the Earth's atmosphere, they become completely evaporated, and the condensation of the gas cloud thus formed may give rise to spherules.

A theoretical study of the condensation of the gas cloud (Ref. 4) shows that, when the expansion of the cloud is not too fast, the dimensions of the condensate particles are proportional to the initial linear dimensions of the evaporated body (proportional to the cubic root of the mass) and rapidly decrease as the initial temperature increases. When the cloud of iron vapor becomes condensed, the condensate particles may be up to 1 μ in size, even if the mass of the vaporized matter is small, e.g., on the order of 1 g. /105

In other cases, the mass and the speed of micrometeorites may be such that they melt during their entry into the atmosphere, and lose speed to the extent that they fall to the Earth in the form of solidified droplets (spherules) under the influence of the gravitational force [5, 6].

When larger meteorites pass through the atmosphere, only their surface layers become heated and melt. The melted layers are blown off the surface by the air flowing past the meteorite and rapidly solidify, mainly in the form of spherules [7, 8].

Along with the melting and blowing off of the surface layer, vaporization of matter also occurs, and this creates conditions for the formation of spherules by the condensation method.

The relative role of various processes involved in the formation of spherules taking place during the passage of meteorites through the Earth's atmosphere is not completely clear, and investigators disagree among themselves as to which process is of the most basic importance.

The composition of the spherules formed during such processes unquestionably reflects to some extent the composition of the initial body. There, however, is a considerable redistribution of elements, which may result in a substantial change of both the mineral and chemical composition of spherules as compared with the initial body.

An investigation of the cosmic spherules separated from the soil in the region of the Tungusk fall of 1908 permits us to characterize their morphology, as well as the mineral and chemical composition. It also permits us to clarify a number of relationships which hold for the formation of spherules in the Earth's atmosphere.

In the case of the Tungusk fall, the formation of spherules probably took place by both the condensation method and as a result of the solidification of the melted substance. At the same time, the morphological characteristics of the spherules found indicate that the latter were formed as a result of the solidification of melted droplets and did not pass through a gas phase. Apparently, the condensation spherules, being of a smaller size, were blown into the upper layers of the atmosphere during the explosion of the Tungusk meteorite and fell chiefly outside the region under investigation. A search for such condensation spherules was not conducted, since the procedure in use could only distinguish particles of larger dimensions.

The chemical analysis of spherules 50-300 μ in diameter and 0.001-0.1 mg in weight, done by M. N. Petrikova [10] using the ultramicroanalysis method, shows that dark magnetic spherules consist mainly of iron oxides; the iron content in them is about 2/3 of the weight of the spherule. In a number of cases when the iron content was substantially lower than that indicated above, there was a skeleton residue, probably of silicate composition, which was insoluble in acids.

Many dark magnetic spherules have a low nickel content (<1%). Those spherules in which the external features indicate the presence of a metal core have a much greater nickel content (>7.5%).

The investigation of the distribution of elements inside the spherule was done by N. P. Il'in using the method of X-ray microanalysis of polished spherule segments on the RSASh-2 device [10].

The results of the analysis are shown in the table.

For spherules containing metal cores (Fig. 1) it is quite characteristic to see a sharp increase in the nickel content of the core, amounting to 90%, with a simultaneous lower nickel content in the oxide layer. Similar changes in the cobalt content occur, but are less pronounced.

TABLE 1

RESULTS OF X-RAY SPECTRAL MICROANALYSIS OF THE MAGNETIC SPHERULES FROM THE REGION OF THE TUNGUSK FALL

	Spherule	Diameter	Fe	Ni	Co	Ir
			Content			
1.	Core	40	22	76	1.4	99.4
	Shell	160	72	2.2	0.2	74.4
2.	Core	70	10	90	1.6	101.6
	Shell	172	71	2.3	0.4	73.7
3.	Without core	296	68	4.4	0.4	72.8
4.	Without core	276	66	7.3	0.4	73.7
5.	Without core	186	69	3.3	0.3	72.6
6.	Without core	220	66	4.4	0.3	70.7

The process of selective oxidation of nickelous iron accompanied by an increase of the nickel content of the metallic phase is well known in metallurgy. A similar effect in cosmic spherules was first observed by Castaing and Fredriksson [11] who noted that the maximum nickel content of the spherule core was up to 53%. Studies of spherules obtained from the region of the Tungusk fall indicate that this content may be much higher.

The distribution of elements in the spherules that do not contain cores (Fig. 2) may be very uniform over the cross-section.

In order to investigate the processes resulting in a difference in the chemical composition of cosmogenic spherules and in the diversity of their morphological forms, we have done a series of experiments which reproduced the formation of spherules of various composition.

Thus, in order to study the behavior of iron, nickel, and cobalt during the processes occurring when ferrous meteorites passed through the Earth's atmosphere (fast heating - melting - oxidation and blowing off of the melted

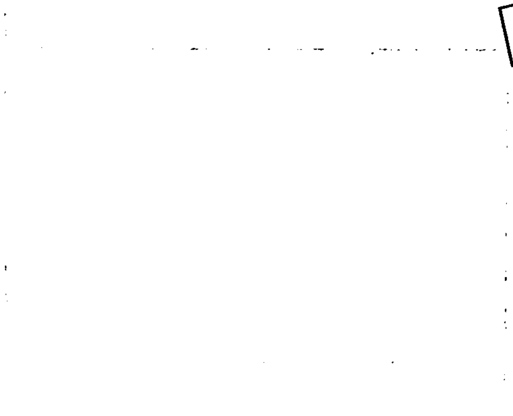

Figure 1. Polished section of a magnetic spherule with a metal core. The spherule diameter is 160 μ; core diameter is 40 μ.

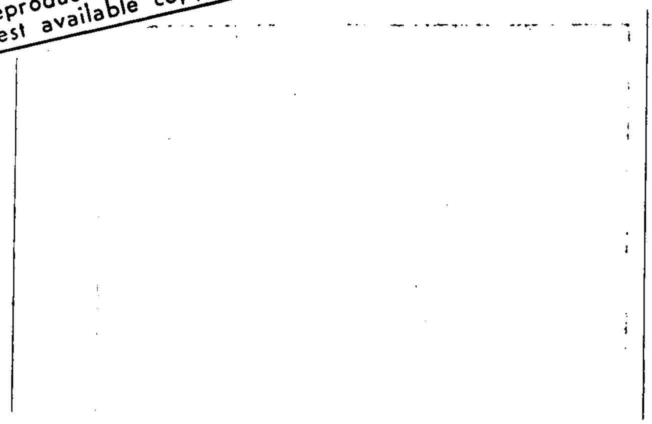

Figure 2. Polished section of a magnetic spherule 296 μ in diameter.

substance from the surface - solidification of the droplets thus formed in the form of spherules), a body of cylindrical shape and of iron-nickel alloy (the initial composition was 89% Fe, 10% Ni, 1% Co) was put in the flame of an oxygen-acetylene burner at the temperature of about 2000°C.

As a result of the solidification of blown-off droplets in the air, /107
magnetic spherules were obtained which were morphologically similar to those found in the region of the Tungusk fall. Hollow forms were frequently encountered.

It is important that the nickel content in the spherules obtained according to ultramicrochemical analysis was as a whole in all cases investigated lower than its content in the initial alloy. In a majority of objects, the nickel content ranged from 3.5% up to the resolution limit of the method, and only in two spherules it is, respectively, 6.5 and 9%.

The X-ray spectral microanalysis showed that for artificial spherules consisting of the metal core and an oxide shell there was a much higher nickel content in the metal phase as compared with the oxide shell. Thus, the metal core of one of the spherules thus obtained consisted of 83% Fe, 15% Ni, 2% Co as compared with 72% Fe, 0.2% Ni, 0.1% Co in the oxide shell.

During the melting and partial oxidation of the meteoritic iron as a result of ablation during the passage through the atmosphere, the element distribution between the metal and oxide phases is basically controlled by the "affinity" of the elements to oxygen, i.e., by the free energy of the corresponding oxides — ΔZ (in kcal per gram/ atom of oxygen) [12]:

Element	At 1000° K	At 2000° K	Element	At 1000° K	At 2000° K
TiO_2	91	70	Fe_2O_3	45	--
MnO	75	55	CoO	38	16
Cr_2O_3	68	49	NiO	37	15
FeO	47	32	Cu_2O	23	10

The elements that have lower affinity to oxygen than iron (lower values of — ΔZ of the oxides) will enrich the metal phase, and the elements with a higher affinity to oxygen will accumulate in the oxide shell.

As we can see from the above data, copper, nickel, and cobalt should concentrate in the metal phase, whereas titanium, manganese, chromium should enrich the oxide phase. The above data on the distribution of nickel and cobalt in the magnetic spherules from the region of the Tungusk fall and in the artificial spherules are a good illustration of the preceding statement, and show that the degree of separation of elements during rapid fusion and oxidation may be very high.

Undoubtedly, during ablation in the atmosphere of a cosmic ferrous body of uniform composition, the composition of the solidified droplets strongly depends on the relationship between the rates of diffusion and oxidation of the elements in the surface layer and the speed with which this layer is blown off by the oncoming air stream.

During the oxidation of the metal body, if the rate of diffusion of, for example, nickel exceeds its rate of oxidation, the surface layer of the body will have less nickel, and the next layer will have more, as compared with the original body. With a variable rate of ablation or diverse rates of ablation from various portions of the meteorite, as always happens in reality, depending on which layer is being blown off, the solidified droplets will either have a nickel deficit or nickel excess as compared with the original body, or finally, will have the same nickel content as the original body if the rate at which they are blown off is extremely large, and the oxidation occurs mainly in the droplet that has become separated.

In addition, the differentiation of matter during oxidation may be accompanied by the separation of matter during a simultaneous vaporization.

Figure 3. Initial stage of gas separation. Gas bubbles are distributed throughout the entire volume of the spherule.

As a result of such processes, one can assume that the composition of the melting core of ferrous meteorites in various stages of formation and in various segments of the regmaglyptic relief is different.

The distribution of other elements is strongly affected by the same parameters, i.e., the free energy and the ratio of the rates at which the processes occur.

What we have said above does not permit us to simply consider the presence (or absence) in the magnetic spherules of some element (Ni, Co, Cu, Mn, Ti, Cr) as a direct criterion enabling us to distinguish spherules of cosmogenic, petrogenic, or technogenic origin.

In the study of the silicate spherules, main attention was given to modeling the details of their formation. The details of this process are best observed during instantaneous heating up to a melting point of the granules of the mineral in question (several tenths of a millimeter in size) and a rapid cooling ("hardening") in various stages of spherule formation. In order to study the process in more detail, use was made of high-speed photography. The modeling of the formation of silicate cosmic spherules, including the melting stages of ferrous silicates, is shown in Figs. 3 - 9.

The experiments involved thin graphite membranes heated by very strong currents (150 — 180A) to a temperature of about 2,000°C. The speed of the process in question was regulated by the strength of the current; the process lasted for several seconds and could be stopped at any stage.

It should be noted that all processes which occur in a small droplet due to the sharp increase in the surface forces are very clearly manifested as compared with the usually studied melting of large masses in crucibles.

During rapid melting, a sharp-angled particle of a mineral instantaneously assumes a spherical shape; this is accompanied by an intensive process of gas separation in the liquid phase. Initially the fine gas bubbles are distributed throughout the entire volume of the spherule which has a foamy structure (see Fig. 3).

Subsequently the gas partially escapes into the atmosphere, and partially collects in a single bubble (see Figs. 4, 5). If we make a cut through this bubble, we observe a typical "bulb" (see Fig. 6) which then melts into a small monolithic spherule.

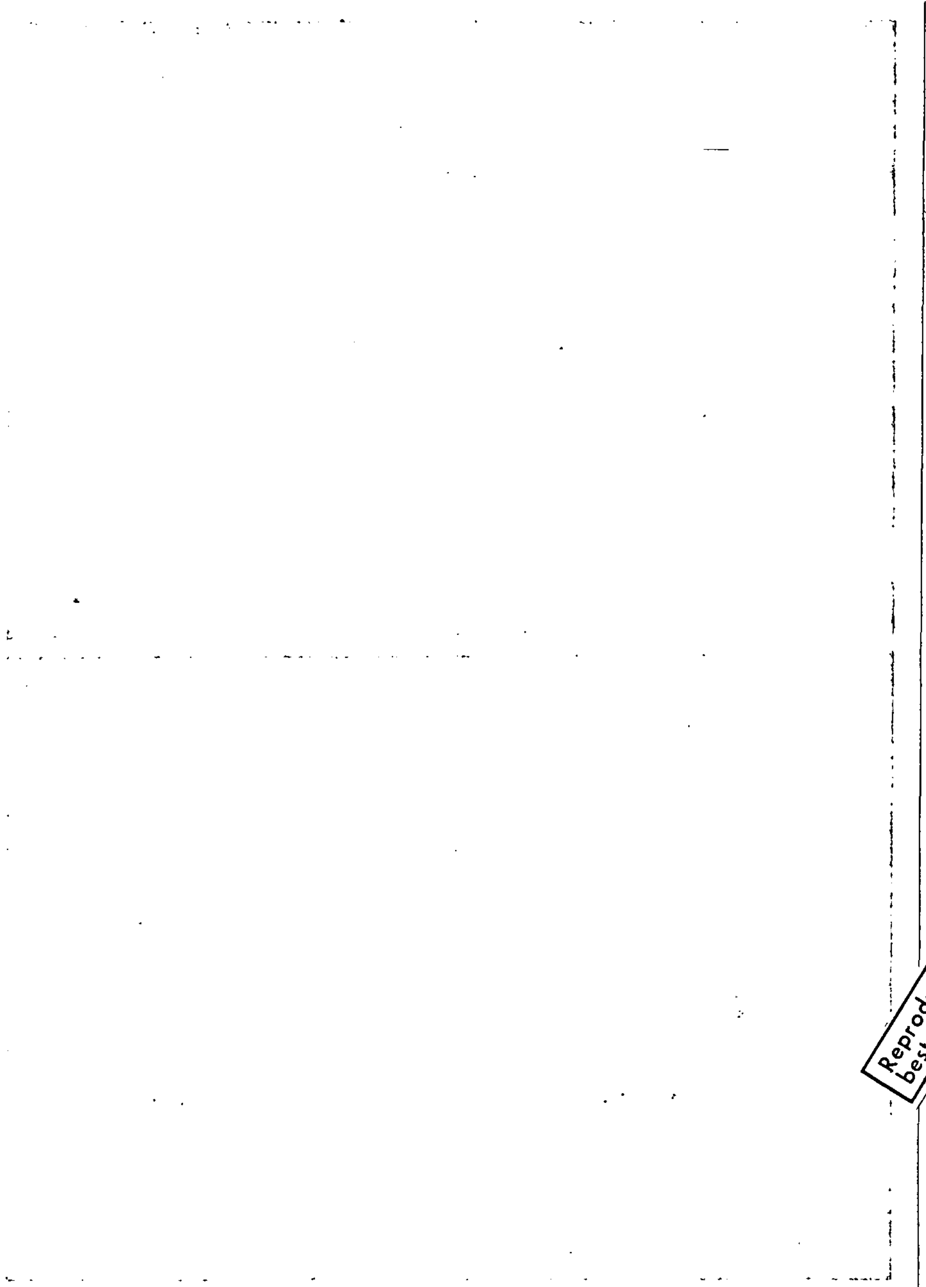

Figure 4 — 5. Continuation of degasification. The gas collects into a single bubble.

One must keep in mind that during a slow heating process, the escaping gases manage to diffuse out of the particle before it becomes solid, and the droplet skips the foam-like stage.

A similar "boiling-up" process as a result of degasification also occurs during the ablation of ferrous meteorites, except that — due to the smaller viscosity of the ferrous melt as compared with the silicate melt — the number of hollow and porous forms will in this case be smaller.

In the ferrous silicate simultaneously with the degasification due to the incongruous melting there also occurs a breakdown of the silicate into two phases: silicate, with a low index of refraction, and magnetic.

The separation of the magnetic phase initially occurs throughout the entire volume of the spherule in the form of tiny dark points (see Fig. 7). Later they accumulate into individual dark spots (see Fig. 6) which combine into droplets, which in the subsequent stage form a single magnetic core.

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Figure 6. Rupture of the gas bubble; formation of the bulb. Dark spots within the bulb represent the nodules of the magnetic phase.

The magnetic core thus formed may be suspended, as it were, inside the gas bubble. Then, when the bubble bursts, a glass spherule forms with an adjoining magnetic spherule (see Figs. 8, 9).

In our experiments, 3 - 4 seconds were enough for the process of differentiation to reach completion.

Figure 7. The initial stage in the separation of the magnetic phase during incongruent melting of the silicate.

The decomposition of ferrous silicate into two phases was observed under these conditions for the silicates of both the pyroxene and olivine series.

The incongruent decomposition of ferrous silicates is substantiated /111 by the darkening of the meteorites, observed during heating and related to the appearance of the metallic phase (Refs. 13, 14). Undoubtedly, the process is strongly affected by the partial pressure of oxygen, and the latter parameter is used, in particular, to determine the composition of the magnetic phase (Ref. 15).

A similar process should also occur during the atmospheric decomposition of stony meteorites.

The decomposition of ferrous silicates at high temperatures can be used to partially explain the formation of complex forms of spherules consisting of silicate and magnetic matter, found in various collections of finely dispersed extraterrestrial matter.

The chemical composition of the magnetic phase, separated as a result of the incongruent melting of meteoric silicates, will have a number of characteristic features.

Figure 8. Final stages of the decomposition into the magnetic and silicate phases.

Figure 9. Final stages of the decomposition into the magnetic and silicate phases. Large silicate sphere with an adjoining small magnetic spherule.

In particular it will be characterized by a nickel and cobalt content. This once again emphasizes the impossibility of using the content of these elements as criteria for the cosmogenic origin of magnetic spherules.

The large viscosity of the silicate melt results in a situation where, among the glass spherules, there should arise more bubbly and foam-like thin-walled formations which disintegrate very easily and need special methods of separation to establish their amount. At the same time, these experiments provide a good explanation for the well-known fact that in the silicate component of extraterrestrial dust there are acid glasses with a low index of refraction (Refs. 16, 17) which does not correspond to the minerals prevalent in stony meteorites.

Thus, the experimental study of the physico-chemical processes accompanying the melting and atomization of meteorites shows that these processes are fairly complex and may result in a substantial differentiation in the finely dispersed matter, in spite of the short lifetime of the phenomenon lasting several seconds.

One should expect more extensive differentiation in the vaporization process of cosmic bodies, followed by the condensation of matter.

The thermodynamic investigation of the process of sublimation and vaporization of a number of simple oxides (Ref. 18) shows that thermal dissociation of compounds occurs during those processes; the composition of the gas phase is distinguished by its complexity and is dependent on temperature. Thus, at the temperature of 3000° K the composition of the gas phase over $S1O_2$ is as follows (in volume percent): S1O — 43.2; 0 — S.0; 0_2 — 39.3; $S1O_2$ — 9.5 The pressure of the gas components at this temperature is approximately 1 ata. The composition of the gas phase over Al_2O_3 at the same temperature is: Al — 21.8; 0 — 51.5; 0_2 — 6.6; AlO — 9.7; Al_2O — 9.9; AO_2O_2 — 0.5. Over MgO, the gas phase at the temperature 3075° K has the composition: Mg — 27.4; 0 — 7.6; 0_2 — 10.0; MgO — 35.0.

Evidently, similar dissociation processes accompany the vaporization of more complex compounds of which the meteoritic bodies are composed.

In addition, the vaporization is accompanied by fractional separation of the chemical components of meteorites according to their volatility. As a result, during the subsequent condensation of matter out of the gas cloud, the composition of the condensate thus formed may be quite different from the original body both in its mineralogical and chemical composition. One should also expect the formation of simpler compounds, including those which are soluble in water.

In this respect, it is of interest to consider studies done by Broka and Pichchiotto (Ref. 19) who investigated the content of various elements in the Antarctic ice. Out of the total nickel content of about 5.10^{-10} g per gram of ice, a greater part of which is in the opinion of the authors of extraterrestrial origin, more than 80% is in a water-soluble form.

These results indicate that there is a necessity of a comprehensive physico-chemical investigation of differentiation and migration of cosmogenic matter in the process of fallout in order to establish its role and development in the geochemical history of assimilation by the Earth.

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